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MIDDLE DISTILLATE FUEL STABILITY CHARACTERISTICS - A  
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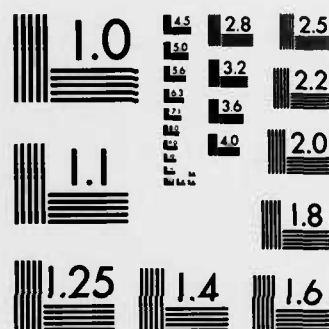
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# MIDDLE DISTILLATE FUEL STABILITY CHARACTERISTICS— A REVIEW

INTERIM REPORT  
AFLRL No. 168

By

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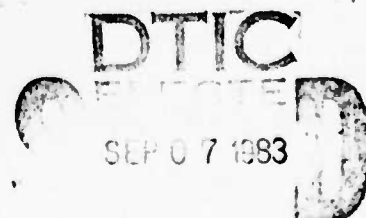
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20. ABSTRACT (Cont'd)

reader may obtain an overview of the current state-of-the-art in fuel stability research. An annotated bibliography has also been included so that more in-depth information may be readily obtained.

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# FOREWORD

The review presented herein was prepared at the U.S. Army Fuels and Lubricants Research Laboratory (USAFRLRL), Southwest Research Institute, San Antonio, Texas, under Contract DAAK70-82-C-0001. The work was funded by the U.S. Army Mobility Equipment Research and Development Command (USAMERADCOM), Ft. Belvoir, VA. Contracting Officer's representative was Mr. F.W. Schaekel, and the technical monitor was Mr. M.E. LePera, Fuels and Lubricants Division, Materials, Fuels and Lubricants Laboratory (DRDME-VF).

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## I. INTRODUCTION

### A. Purpose

The material presented in this review is an accumulation of information from many of the more significant presentations in literature. It is designed to be a ready reference document and, as such, does not contain some of the detailed information that an exhaustive review might cover. However, the inclusion of an annotated bibliography gives a base from which more specific information may be obtained in particular areas of interest.

### B. Historical Information

Petroleum-like bituminous materials were described by Herodotus, Plutarch and others (1)\* 2000 years ago. However, actual use of these materials spans at least 5000 years, dating to the Sumerians, Assyrians, and Babylonians. During those times, seepages were found on the Euphrates River, in Mesopotamia, and in the eastern Mediterranean areas.(2) Crude oil was probably obtained by dipping directly into the seep or by prior digging to enlarge the area and then dipping the material out.(1) Because of these seeps, the area now known as the Dead Sea was, in ancient times, known as Lake Asphaltites, because of the tarballs found on its shores.

The word "petroleum" is attributed to first use by a German mineralogist in a treatise on its recovery and refining published in 1556.(2) Other historical points are noted by Bacon and Hamor.(3)

The tars and oils which made up the substance of petroleum have been used in a wide variety of ways, including caulking, waterproofing, and illumination. In the early 19th century United States, animal fat (especially whale fat) was still the major source of illuminating oil, even though petroleum seeps had been found. With increasing population, a more abundant source of

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\*Underscored numbers in parentheses refer to the list of references at the end of this report.

refined oil became necessary. Distillation of coal was popular, but product volume was not sufficient to overcome the growing needs for less costly and greater volumes of lubricants and illuminating oil. These requirements and the approach of the Industrial Revolution led to completion of the first drilled oil well in the United States at Titusville, Pennsylvania in 1859. Refining of this crude took place in the already existing coal-oil refineries.(2) By 1900, Pennsylvania lubricants had displaced animal and vegetable materials as the primary oil source.(4) By this time, oil fields had been discovered in 14 states, Europe, and the Far East.(2)

From the beginning of this century to the present time, greater emphasis has continually been placed on particular specifications for various refined products. As noted, lubricants and illuminants headed the early product lists; now, approximately 2500 materials are produced, at least in part, from petroleum, not counting the 3000 petrochemicals also produced.(4)

#### C. Processing

Methods for refinement of crude oils have also changed considerably over the years, due to increasing demands for specific products and better overall performance of those products. Several refinery processes are currently in use. Each is generally composed of three fundamental activities:(1)

1. Primary separation of raw materials
2. Preparation of process feed
3. Fractionation of the products

These may be accomplished by:(4)

1. Crude fractionation
2. Thermal decomposition
3. Catalytic cracking
4. Catalytic reforming
5. Hydrocracking

Crude fractionation is generally used as the first step before further processing. Light gasoline, naphtha, kerosene, gas oil, and topped crude are the products obtained from this process.(4) Materials from the process are designated as straight run products. Further refining, as described below, is required for the heavier products.

Successful cracking processes were demonstrated for use in World War I, but it was not until World War II that the thermal cracking process was maximized. Catalytic cracking became successful toward the end of World War II, but its growth has been optimized only within the past 20 years(4), now exceeding thermal cracking in terms of capacity.(5) Thermal cracking treats the feed material at temperatures of 850°-1150°F (454°-621°C) and pressures of 1 to approximately 110 atmospheres for 10 minutes or less. Catalytic cracking requires less severe conditions [750°-1000°F(399°-538°C) at 1-7 atmospheres] while using the catalytic material to accelerate and guide the cracking process to produce the desired final products.(5) Fluidized catalytic cracking (as opposed to the fixed bed process) began in 1942. In this process, vaporized feedstock lifts the powdered catalyst into the reaction bed, thus "fluidizing" the powdered material.

Catalytic reforming is not a popular process in the United States because much higher octane gasoline can be produced by alkylation and catalytic cracking. Reforming also leads to loss of light ends (gases) and therefore is not economically feasible. It does, however, substantially increase the aromatic content of naphthenic feedstock through partial dehydrogenation of the naphthenes.

Hydrocracking produces a final product almost exclusively composed of aliphatic and aromatic materials with little or no sulphur and no nitrogen.(4) This would be the process of choice except for the expense of the hydrogen involved. Even so, use of this process is increasing, and if some of the economic factors are overcome, it could replace catalytic cracking as the major refining process.

#### D. Demand

For FY 1977, the total U.S. petroleum energy demand was approximately 18.6

million barrels per day (of which DOD used 2.6 percent).<sup>(6)</sup> In 1980, total oil consumption in the U.S. was approximately 16.9 million barrels per day.<sup>(7)</sup> During this period (1978) demand for middle distillate fuel oil (diesel, jet fuel, etc.) was approximately 3.4 million barrels per day, or 18 percent of the total demand for that year.<sup>(8)</sup>

#### E. Fuel Stability Background

After a fuel is produced, the time lag prior to end use could vary from weeks to years. Long-term storage stability has been a requirement imposed on military fuels designed for tactical/combat uses.<sup>(9)</sup> However, storage stability (and the prediction of long-term fuel stability) for diesel and distillate fuels has long been recognized as a potential problem by both government and industry.<sup>(10-11)</sup> Many research programs have been undertaken to determine how fuel can be stabilized (by use of additives) as well as what causes degradation to occur (elucidation of reaction mechanisms). Various specifications have been formulated for specific use fuels. These specifications also include geographical allowances, particularly for temperature. A summary of fuel specifications for aviation and diesel fuels is given in Tables 1 and 2.

Almost a quarter of a century ago, the chemical character of fuel degradation products was postulated.<sup>(12)</sup> Well over one-half century ago, it was noted that the presence of diolefinic hydrocarbons in cracked distillates was at least partially responsible for gum formation in gasoline.<sup>(13)</sup> Several papers published in the late 1920's through the 1930's verify and expand upon this fact.<sup>(14)</sup> The following sections summarize current knowledge in the field of middle distillate fuel stability.

## II. MECHANISMS OF GUM FORMATION

#### A. Oxidation/Autoxidation

This mechanism is considered to be the most prominent of the degradation

TABLE 1. SUMMARY OF FUEL SPECIFICATION PROPERTIES  
OF AVIATION TURBINE FUELS

Specification: Product: NATO Code No.:	MIL-T-5624K* Amendment 1		MIL-T-83133A**	ASTM D 1655***	
	Grade JP-4	Grade JP-5	Grade JP-8	Jet A/Jet A-1	Jet B
Properties	F-40	F-44	F-34	--	--
Distillation Temp., °C (D 2887 limits in parentheses)					
10% recovered, max temp	--	205(185)	205(186)	204.4	--
20% recovered, max temp	145(130)	--	--	--	143.8
50% recovered, max temp	190(185)	--	--	--	187.8
90% recovered, max temp	245(250)	--	--	--	243.3
End point, max temp	270(320)	290(320)	300(330)	300	--
Residue, vol%, max (D 86)	1.5	1.5	1.5	1.5	1.5
Loss, vol%, max (D 86)	1.5	1.5	1.5	1.5	1.5
Flash Point, °C(°F), min	--	60(140)	38(100) or 41(105) 1/	37.8(100)	--
Vapor Pressure, 37.8°C(100°F), kPa (psi)	14-21 (2.0-3.0)	--	--	--	--
Freezing Point, °C(°F), max	-58(-72)	-46(-51)	-50(-58)	2/ 8	(3 max) -50
Viscosity, @ -20°C, cSt, max	--	8.5	8.0	8	--
Water Reaction,					
Interface rating, max	1b	--	1b	1b	1b
Separation rating, max	1	--	--	2	2
Water Separation Index, mod., min	70	85	3/	--	--
Total Acid No., mg KOH/g, max	0.015	0.015	0.015	0.1	--
Aromatics, vol%, max	25.0	25.0	25.0	20 4/	20 4/
Olefins, vol%, max	5.0	5.0	5.0	--	--
Mercaptan Sulfur, wt%, max	0.001	0.001	0.001	0.003	0.003
Sulfur, total wt%, max	0.40	0.40	0.3	0.3	0.3
Copper Strip Corrosion, 2 hr @ 100°C (212°F), max	1b	1b	1b	No. 1	No. 1
Density, kg/m <sup>3</sup> , min (°API, max), @ 15°C	751(57.0)	788(48.0)	775(51.0)	775.3(51)	750.7(57)
Density, kg/m <sup>3</sup> , max (°API, min) @ 15°C	802(45.0)	845(36.0)	840(37.0)	839.8(37)	801.7(45)
Thermal Stability (JFTOT), Change in pressure drop, mm of Hg, max	25	25	25	25	25
Preheater deposit code, less than	3	3	3	3	3
Existent Gum, mg/100 mL, max	7.0	7.0	7.0	7	7
Particulate Matter, mg/liter, max 8/	1.0	1.0	1.0	--	--
Filtration Time, minutes, max 8/	15	--	--	--	--
Heating Value, Aniline-gravity product, min, or Net heat of combustion, MJ/kg (Btu/lb), mi	5,250 42.8(18,400)	4,500 42.6(18,300)	-- 42.8(18,400)	-- 42.8(18,400)	-- 42.8(18,400)
Hydrogen content, wt%, min, or	13.6	13.5	13.5	--	--
Smoke point, mm, min, or	20.0	19.0	25	25	25
Smoke point, mm, min, and	--	--	19	20	20
Naphthalenes, vol%, max	--	--	3.0	3	3
Fuel System Icing Inhibitor, vol%	0.10-0.15	0.10-0.15	0.10-0.15	--	--
Fuel Electrical Conductivity, pS/m	--	--	200-600	50-300 5/	50-300 5/

\* Dated 12 November 1976

\*\* Dated 5 May 1976

\*\*\* Dated 1978

- 1/ The minimum flash point shall be 38°C as measured using ASTM D 3243 and 41°C as measured using ASTM D 93.
- 2/ The maximum freezing point for Jet A is -40°F and for Jet A-1 it is -50°C (-58°F).
- 3/ The minimum water separation index, modified, rating shall be 85 for JP-8 fuel without both the corrosion inhibitor and the electrical conductivity additives present OR 70 for JP-8 fuel containing all required additives except for the electrical conductivity additive.
- 4/ Jet A with an aromatics content over 20 volume % but not exceeding 25 volume % and Jet A-1 or Jet B with an aromatics content over 20 volume % but not exceeding 22 volume % is permitted provided the supplier (seller) notifies the purchaser of the volume, distribution and aromatic content under conditions mutually agreeable to both parties. This footnote is subject to reapproval in 1979.
- 5/ Applies only when an electrical conductivity additive is used.

TABLE 2. SUMMARY OF FUEL SPECIFICATION PROPERTIES OF DIESEL AND DISTILLATE FUELS

Specification: Product: NATO Code No.:	VV-F-800C*				MIL-F-16884C***		MIL-F-24397****	
	DF-A	DF-1	DF-2 CONUS	DF-2 OCONUS	DF-M	F-76	ND	ND
Distillation, °F(°C)								
50% evaporated, max	Report	Report	Report	Report	--	--	644(340)	
90% evaporated, max	550(288)	550(288)	640(338)	675(357)	675(357)	675(357)	740(393)	
End point, max	572(300)	626(330)	700(370)	700(370)	725(385)	725(385)	--	
Residue, vol%, max	3	3	3	3	3	3	--	
Flash Point, °F(°C), min	100(38)	100(38)	125(52)	133(56)	140(60)	140(60)	150(66)	
Cloud Point, °F(°C), max	-60(-51)	2/	2/	2/	30(-1)	30(-1)	--	
Pour Point, °F(°C), max	Report	Report	Report	3/	20(-7)	20(-7)	25	
Viscosity @ 104°F(340°C), cSt	1.1-2.4	1.3-2.1	1.1-4.1	1.8-9.5	1.8-4.5	1.8-4.5	10 max	
Viscosity @ 68°F(20°C), cSt	--	--	--	--	--	--	--	
Total Acid Number, mg KOH/g, max	0.05	--	--	0.10	0.10	0.30	--	
Sulfur, % wt., max	0.25	0.50	0.50	0.70	0.7	1.00	1.30	
Copper Strip Corrosion, 3 hrs @ 122°F(50°C), max	3	3	3	1	1	--	--	
3 hrs @ 212°F(100°C), max	--	--	--	--	--	--	2	
Ash, % wt., max	0.01	0.01	0.01	0.02	0.005	0.005	0.01	
Gravity, °API	Report	Report	Report	32.9-41.0	Record	Record	27 min	
Density @ 15°C, kg/L	--	--	--	0.815-0.860	0.815-0.860	--	--	
Accelerated Stability, total Insolubles, mg/100 mL, max 4/	1.5	1.5	1.5	1.5	2.5	--	--	
Water & Sediment, % vol, max	0.01	0.01	0.01	0.01	--	--	0.02	
Carbon Residue on 10% bottoms, % wt., max 5/	0.10	0.15	0.35	0.20	0.2	0.2	0.4	
Particulate Contamination mg/L, max	10	10	10	10	--	--	--	
Cetane Number, min	40	45	45	45	45	45	39	
Appearance, visual	--	--	--	--	Bright and Clear	Bright and Clear	--	
Color (ASTM D 1500), max	--	--	--	--	3	3	--	
Demulsification, min, max	--	--	--	--	5	10	--	

\* Dated 15 September 1980.

\*\* From Annex C to STANAG 2845, 21 September 1978.

\*\*\* Amendment 1 dated 22 March 1978.

\*\*\*\* Cancelled 23 May 1977.

1/ DF-2 intended for entry into the Central European Pipeline System shall have a minimum value of 58°C.

2/ DF-2 destined for Europe and S. Korea shall have a maximum limit of 9°F(-13°C).

3/ DF-2 destined for Europe and S. Korea shall have a maximum limit of 0°F(-18°C).

4/ This requirement is applicable only for military bulk deliveries intended for tactical, OCONUS, or long term storage (greater than six months) applications (i.e., Army depots, etc.).

5/ See Appendix of VV-F-800C. The maximum limits do not apply for samples containing cetane improvers. In those instances, the test must be performed on the base fuel blend.

mechanisms since air ( $O_2$ ) is normally present at all times and temperatures. The mechanism for oxygen addition to organic compounds, particularly diolefins, appears to be well agreed upon.(15-18) The reaction is free radical in nature with an oxygen molecule adding to the host hydrocarbon, forming a peroxy radical which can then reform to either a hydroperoxide or a dialkylperoxide. From this point, polymerization may occur, forming the gums.

## B. Acid/base Reactions

### 1. Sulfur Compounds

Certain materials, such as the polysulfides, have been shown to have a greater effect on gum formation than either mercaptans or thiophenols.(19) Other studies(20,21) using various sulfur compounds in conjunction with 2,5-dimethylpyrrole (stability decriaser) showed that the synergistic properties were different than the properties of the sulfur compounds alone. For example, sulfide compounds had little effect on sediment formation, while thiols showed inhibitory effects and sulfonic acids acted to increase sediment formation.

### 2. Nitrogen Compounds

Organo-nitrogen compounds and their effect on fuel storage stability have been the subject of many studies.(19-26) A large number of nitrogen compounds have been shown to have no effect or even an inhibitory effect on certain gum-forming reactions. However, 2,5 substituted pyridines and 2,5 substituted pyrroles have been shown to be quite active in sediment formation, particularly when the latter compound is placed in the fuel prior to aging the sample.

## C. Metal Catalysis

Certain metals, when in solution, behave as catalysts for on-going reactions, particularly the decomposition of hydroperoxides to free radicals.



For example: (18)



or (16)



Iron and nickel also act in a manner similar to that illustrated for copper above.

#### D. Polymerization/Condensation

There are two types of polymerization reactions: (1) addition (free radical and ionic), and (2) condensation. Addition reactions occur through coupling of complete molecules to form a larger molecule. Condensation occurs with the loss of some product, usually water.

Polymerization requires the presence of a small amount of initiator (usually a peroxide). The difference between this type of reaction and autoxidation is that the final product does not necessarily include oxygen.

Examples of a condensation reaction are that which occurs between carboxylic acids and amines to yield amides or acid/alcohol to yield esters. If both components have more than one functional group, polymerization can occur. (27)

#### E. Biological Activity

The effect of biological growth in fuel systems can be considered as causing fuel degradation from two points of view. The first actually does not cause chemical transformation of the fuel components but as the microbes grow, they form particulate matter or a film-like colony which can cause filter and/or injector fouling. The second mode of degradation is from the acidic nature of the growth byproducts. This change in pH can affect either the container (metal solubility), thus increasing potential catalytic activity or act as an initiator for a polymerization reaction (see above). Although

many types of fungal and bacterial growth have been observed in fuel tanks and on filters, the overall most abundant is the fungus Cladosporium resinae. Examples of common yeasts and bacteria are Candida and Pseudomonas aeruginosa, respectively. (28-33).

### III. REACTION PRODUCT COMPOSITION

One of the first postulations of a "typical" sediment molecule is shown in Figure 1.(12) Variations in this structure are also suggested by replace-

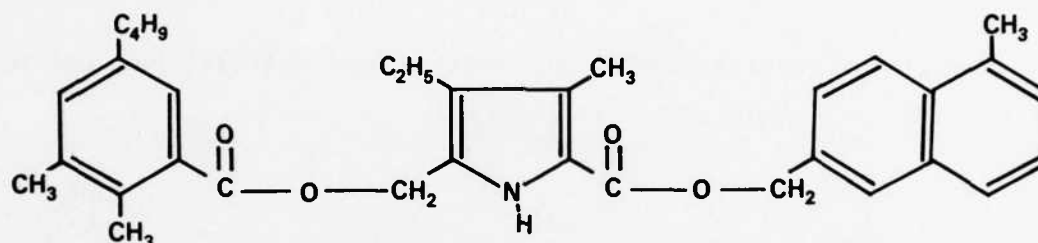


FIGURE 1. TYPICAL SEDIMENT MOLECULE

ment of one or more of the three ring groups with other components. The ester linkage remains present in each form. Some of the products resulting from reaction of 2,5 dimethylpyrrole are given in Figure 2.(23)

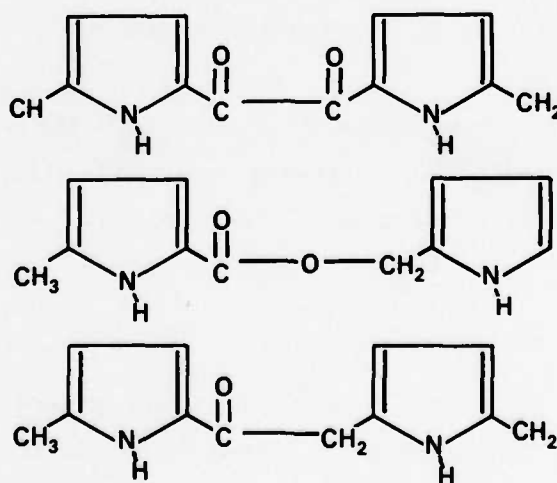


FIGURE 2. PRODUCTS FROM THE REACTION OF 2,5-DIMETHYLPYRROLE

TABLE 3. ELEMENTAL ANALYSIS OF GUMS

Element	Gums From Heating Oil(10), %	Gums From Gasoline(17), %
C	60-78	70-80
H	6.0-7.5	7-10
N	1.5-2.8	0.2
S	0.9-3.6	0.4-3
O	7.4-17.5	10-20

The empirical formula developed from averaging the above data is  $C_{6.3}H_{7.0}NO_{1.67}$ . Elemental analysis has also been performed on various gums. The results of these analyses are shown in Table 3.

The involvement of sulfur in the analysis of gum material has led to the postulation of the formula shown in Figure 3.

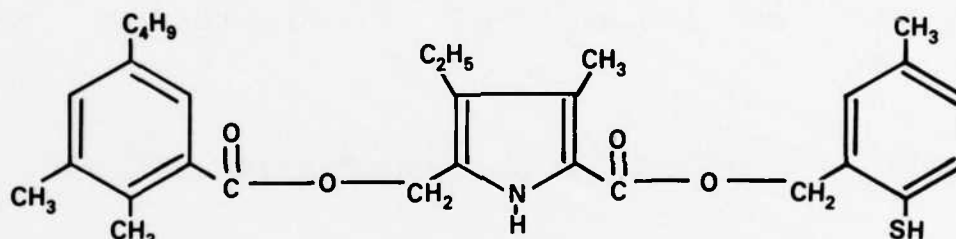


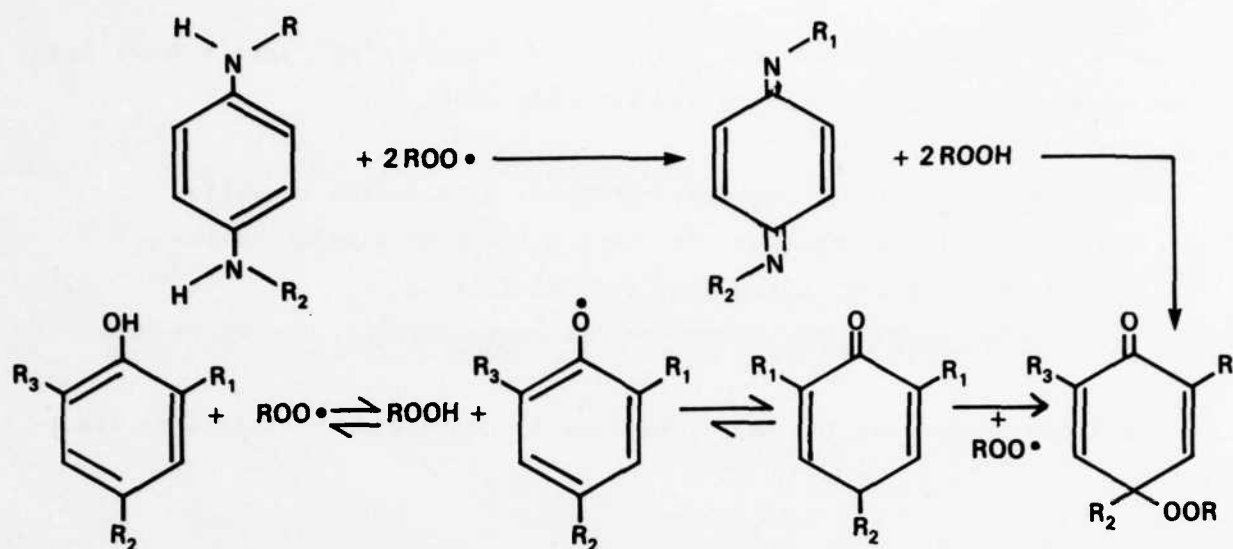
FIGURE 3. SEDIMENT MOLECULE

#### IV. FUEL STABILIZERS/ENHANCERS

The preceding discussion has concerned itself with the degradation of neat, middle distillate fuels. The following sections will be concerned with methods by which that degradation may be controlled.

##### A. Antioxidants

To prevent oxidation of a fuel, it is normally considered that a "chain-breaking" molecule or free radical "scavenger" needs to be employed. Phenylene diamines or hindered phenols are most commonly used for this purpose. The reactions which occur are:(18)



#### B. Dispersants

Particulate material, whether derived from fuel decomposition or external sources, can agglomerate to form still larger particles, which may eventually clog filters, fuel lines, and/or injector nozzles. In order to maintain a minimum of particles of large size, surfactants are employed to prevent settling. Generally, nitrogen-based chemicals are the better materials of choice. Oleoylamide is a good example. Salts of alkylbenzenesulfonic acid may also be used. To be effective, the amount of dispersant used must be in excess of that required; otherwise, it will be depleted and settling of particulates will reoccur.

#### C. Metal Deactivators

Elimination of the catalytic effect of dissolved metals may be effectively accomplished through addition of chelating materials to the fuel. A common chelating agent is  $N,N'$ -disalicylidene propylenediamine.

#### D. Sweetening

Product quality in general may be improved by treatment of the original crudes prior to further processing. For many years, a sulfuric acid wash

followed by aqueous alkali and addition of "sweetening" agents have been used. Four sweetening processes are commonly used.

1. Doctor process: Requires treatment with sodium plumbite.
2. Lead sulfide process: Involves a reaction similar to the doctor process, using lead sulfide instead.
3. Copper sweetening: Involves treatment with cupric chloride.

In the above processes, the major reaction is conversion of thiols to disulfides.

4. Merox process: The newest of these processes, this process follows use of a chelate catalyst(4) which allows this process to be used either as a sweetening agent or solvent extraction process.

## V. METHODS USED TO STUDY FUEL DECOMPOSITION MECHANISMS

### A. Accelerated Decomposition

Many methods have been used to accelerate or "test" the ability of any given fuel to degrade. It is normally assumed that the prevailing mechanism is that of oxidation. The following procedures are most commonly employed.(29)

- |                      |                           |
|----------------------|---------------------------|
| 1. Storage at 43.3°C | 4. ASTM D 873 (modified)  |
| 2. Storage at 80°C   | 5. ASTM D 2274 (modified) |
| 3. Storage at 150°C  | 6. ASTM D 3241 (modified) |

The first three procedures may be carried out for any time duration of interest; normally, the higher the temperature, the shorter the time of experiment, e.g., 43.3°C maximum 6 months to 1 year, 150°C usually <10 hours. The containers, normally borosilicate glass, may be vented to the atmosphere, or sealed under nitrogen or any other gas as per study emphasis.

ASTM D 873 (modified) requires a volume of filtered fuel to be aged at 100°C for 16 hours under 100 psi oxygen.

ASTM D 2274 (modified) requires a volume of filtered fuel to be aged at 95°C for 16 hours at ambient pressure with oxygen continuously bubbled through the sample.

ASTM D 3241 (modified), also known as the jet fuel thermal oxidation test (JFTOT), requires a volume of filtered fuel to be pumped past an electrically heated metal tube, then through a 17- $\mu$ m filter across which the pressure drop is measured.

In each of the above methods, "insoluble" particulates are measured by passing an aliquot of the aged fuel through a preweighed filter. The modification noted generally indicates a change in nominal pore size of this filter; usually 0.8  $\mu$ m rather than the specified 1.2  $\mu$ m. Adherent gums are dissolved in toluene-acetone-methanol (TAM) after a prewash with heptane. The TAM solution is then placed in a preweighed beaker and the solvent evaporated. Soluble gums may be determined by the steam jet or air jet process.

## B. Correlation Between Acceleration Techniques

### 1. Experimental Results

The techniques listed above, plus storage at 93.3°C in a soft glass container and a chromic acid oxidation test, were employed in an extensive matrix involving six test fuels.<sup>(34)</sup> Each fuel was evaluated for particulates (adherent and suspended), steam jet gum, color, light absorbance and acid number.

The Pearson Product-Moment correlation coefficient was calculated with major emphasis on total insolubles, steam jet gum, and total gum. The overall conclusion reached in this study was that the 43.3°C storage data did not follow a trend predictable by any one of the other test methods. However,

the 80°C test appeared to yield the closest prediction. Reference 19 also details the results of an extensive correlation test matrix with the conclusion that significant correlations are minimal.

There are several possible reasons for this. First, different reaction mechanisms may predominate at different temperatures, particularly above 160° to 180°F (71° to 82°C). Also, as temperature increases, thermal degradation, rather than oxidation, becomes the predominant mechanism. Secondly, filtration and comparison of material retained on the filter presuppose that particle size is reproducible from one experiment to the next; however, there are no published studies yielding information on this point. Other possible reasons for the variability may be sample volume (surface to volume ratio), type of filter used, flow rate through the filter, methods of drying the filters, temperature required for sample workup (particularly steam jet gum), etc. Many of these variables could be eliminated by procedural change and subsequent verification of the resulting experiments. It is obvious that, at this time, each of the tests listed must be interpreted on an individual basis, with the results perhaps being valid within a range rather than as a specific number.

## 2. The Arrhenius Equation

Attempts to predict correlative temperatures may also be undertaken in a theoretical sense. The equation needed for this prediction is based on the one developed by Arrhenius;  $k = Ze^{-E_a/RT}$  where  $E_a$  is the energy of activation,  $R$  is the gas constant, and  $T$  is the temperature. Including a pressure correction term (for accelerated aging due to increased ambient pressure such as in a bomb) and assuming that  $k$  is proportional to  $\frac{1}{t}$  and integrating, the equation becomes(19)

$$\ln \frac{t_1}{t_2} = A\left(\frac{1}{T_1} - \frac{1}{T_2}\right) + B \ln \frac{P_1}{P_2}$$

The term  $A$  equals  $E_a/R$  where  $R = 1.9869 \text{ cal}(15^\circ)/^\circ\text{C mole}$ , and  $t$  is the time required for a specific amount of material to be formed. By rearrangement, the equation may also be used to predict amounts of material that will be formed in a given time and assuming that  $P_1/P_2 \approx 1$ :(21)



$$\ln \frac{M_2}{M_1} = A \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$$

where M is the amount of material formed.

Several values have also been suggested for the energy of activation.

<u>Type of Fuel</u>	<u>Ea (<math>\frac{\text{kCal}}{\text{mole}}</math>)</u>
Jet fuels	21.0(19), 10.0(34)
#2 Diesel	10.7(21)
JP-8	14.4(21)

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terious products in middle distillate fuels; and apply the results toward development of more reliable test methods for fuel stability. During first year, eight accelerated stability tests were chosen and evaluated using a set of 6 test fuels. During the second year, primary emphasis was placed on testing 43°C and 150°C tests which are being cooperatively developed by ASTM. In general, test results at 43°C, 80°C, 150°C, and ASTM D 2274 provided directional agreement. In an effort to standardize the 43°C and 150°C tests, planning and cooperative testing was provided to ASTM Committee D-2, Technical Division E-V.

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49. Taylor, W.F. and Wallace, T.J., "Kinetics of Deposit Formation From Hydrocarbon Fuels at High Temperatures," I&EC Product Research and Development, 6, (4), December 1967.

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50. Trayser, D.A., et al., "Final Report--Deterioration of Fuels and Fuel-Using Equipment," Battelle Memorial Institute, August 1967.

This report covers the results of studies which were aimed at estab-

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51. Vere, R.A., "Fuel Composition Data From Deposit Analysis," CRC Group on Oxidation Stability of Gas Turbine Fuels Symposium on Jet Fuel Stability, 30 April 1981.

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A laboratory test rig has shown more highly refined fuels to have poorer lubricity. A 10 to 20 percent blend of conventional treated fuel improves lubricity to normal. Addition of highly polar compounds from conventionally treated fuels significantly improves lubricity.

53. Vilyanskaya, E.D., et al., "New Conditions in Test Method for Determining Thermal-Oxidative Stability of Inhibited Turbine Oils," Chemistry and Technology of Fuels and Oils, 17 (3-4) 1981.

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IR spectra of fuels and deposits were obtained for heating oil and Jet A fuels.



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This report details the development of a portable device to measure the cleanliness and stability of diesel fuels in both bulk and vehicle fuel cell storage.

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The influence of substituted pyridines, pyrroles, indoles, and quinolines on storage stability of conventional Jet A turbine fuel is evaluated.

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How the contents of total and basic nitrogen in straight-run petroleum cuts are related to the average boiling point of the cut is presented.

## GLOSSARY OF TERMS

1. Additive - A chemical agent employed to assure the presence of certain desirable characteristics in fuels or other materials.
2. Adherent gum - See insoluble gum.
3. Barrel - A unit of measure fixed for certain commodities (42 gallons for petroleum).
4. Bituminous - Resembling or containing various mixtures of hydrocarbons (a tar) often together with their nonmetallic derivative.
5. Break point - 1) The time at which the rate of formation of insoluble particulates significantly increases compared to the induction period.  
2) The time at which the weight of filterable particulates exceeds a specified value by 20 mg/100 mL.
6. Crude - Unrefined petroleum.
7. Diesel fuel - A hydrocarbon fuel used in diesel engines.
8. Distillate fuel - A fuel obtained by distillation of crude materials into fractions according to temperature.
9. Existent gum - The evaporation residue of aircraft fuel or heptane-insoluble portion of the evaporation residue of motor gasoline.
10. Free radical - An atom or group of atoms possessing an unpaired electron normally formed by cleavage of the parent molecule.
11. Gum - Varnish-like, tacky, noncombustible deposits formed during deterioration of petroleum and its products.
12. Insoluble gum - Deposit adhering to the sample container after removal of the aged fuel.
13. Petroleum - A complex oily, flammable liquid mixture composed of hydrocarbons and small amounts of other substances which may vary from almost colorless to black.
14. Potential Gum - The sum of soluble and insoluble gum.
15. Precipitate - Sediment and suspended material with aged fuel.
16. Sediment - Foreign particulate matter which settles to the bottom of a storage container.
17. Soluble gum - Deterioration products existing in solution in the aged fuel and the benzene-acetone soluble portion of the deposits on the container wall. Determined by air jet gum method.

18. Storage Stability - Resistance of a fuel to spontaneous formation of deleterious products when stored over long periods of time.
19. Tar - A dark odorous, viscous liquid obtained by destructive distillation of organic material.
20. Thermal stability - Relating to the tendency to form deposits at high temperature.
21. Total potential residue - Sum of the potential gum and precipitate.
22. Unwashed gum - The evaporation residue of motor gasoline consisting of existent gum and non-volatile additive components.

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